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(54) **Sealed seams for waterproof, water vapour permeable article**

(57) Proposed is a process for sealing the seams of a water vapour permeable article comprising a waterproof, water vapour permeable film and having seams, wherein a surface of the article is contacted at least at the seams of the film with a coating solution of a hydrophilic polymer in an organic solvent which acts as a swelling agent for the waterproof, water vapour permeable film, after which the solvent is evaporated. Preference is given to a process wherein the contacting comprises dipping the film into the coating solution and the article is a lining comprising a laminate of a waterproof, but water vapour permeable film and a textile material.

The water vapour permeable film in the laminate preferably is made of a hydrophilic copolyetherester or copolyetheramide, while the hydrophilic polymer soluble in an organic solvent preferably is a copolyetherester.

Also claimed is a waterproof, water vapour permeable article having seams sealed with the invented process and which is shaped as a glove, garment or shoe.

EP 0 974 696 A1

Description

5 [0001] The invention pertains to a process for sealing the seams of a waterproof water vapour permeable article comprising a waterproof, water vapour permeable film and having seams, and to a waterproof, water vapour permeable article comprising a waterproof, water vapour permeable film having sealed seams.

[0002] Such a process is known from EP-A-410 291. The waterproof, water vapour permeable article disclosed in said document comprises a waterproof insert for lining the interior of contoured articles of clothing, which comprises two superimposed layers, each of which is a laminate composed of a sheet of porous polymeric membrane that is breathable but waterproof laminated by an adhesive of breathable thermoplastic polymer to a sheet of a textile material.
 10 According to the process disclosed therein, first a laminate is produced by bonding a textile material and a water vapour permeable film together using a waterproof, but water vapour permeable adhesive applied across the entire surface area, after which sections of this laminate with the textile sides facing each other are heated following the contours of the material to be lined, so that the adhesive will melt *in situ* and/or is activated, and after cooling a lining with wholly waterproof seams is obtained.

15 [0003] A drawback to the process described in this document is that a thermoplastic polyetherurethane is selected as the adhesive. A significant disadvantage of polyurethanes is constituted by the high toxicity of the polyisocyanates employed in their preparation and the long periods required for the adhesive to complete its reaction process.

[0004] The invention now provides a process which obviates the drawback to the known process wholly or for the most part.

20 [0005] The invention consists in that in a process of the known type mentioned in the opening paragraph a surface of the article is contacted at least at the seams of the film with a coating solution of a hydrophilic polymer in an organic solvent which acts as a swelling agent for the waterproof, water vapour permeable film, after which the solvent is evaporated.

[0006] A major advantage achieved when using the process according to the invention is that the article is ready for use immediately after evaporation of the solvent and can be processed without delay.

[0007] A preferred method consists in that the contacting comprises dipping the film into the coating solution. Thus far, especially good results have been obtained with the article being a lining comprising a laminate of the waterproof, water vapour permeable film and a textile material.

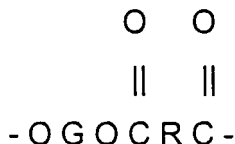
The invented process further comprises, prior to the contacting step, joining together along contours of a material to be lined one or more sections of the lining in which textile sides of the lining are facing one another.

30 [0008] It is not necessary to treat the entire lining with a solution of a hydrophilic polymer. Preferably, only the section of the lining with the waterproof film turned inside out where the seams are is subjected to a dipping treatment.

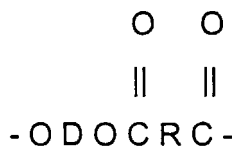
[0009] The linings of which the seams can be waterproofed by the process according to the invention are used not only in the textile industry but also in the furniture and car industries. However, the advantages are especially evident in the case of use in the clothing industry in the manufacture of waterproof, but water vapour permeable gloves, garments or shoes.

[0010] It has been found that, as a rule, very favourable results are obtained when

40 a) for the water vapour permeable, but waterproof film in the laminate use is made of a copolyetherester consisting of a plurality of recurrent intralinear long-chain ester units and short-chain ester units randomly joined head to tail through ester bonds, the long-chain ester units corresponding to the formula



50 and the short-chain ester units corresponding to the formula:



wherein G is a divalent radical remaining after the removal of terminal hydroxyl groups from at least one long-chain glycol having an average molecular weight in the range of 600 to 4000 and an atomic ratio of carbon to oxygen in the range of 2,0 to 4,3, at least 20 wt.% of the long-chain glycol having a carbon to oxygen ratio in the range of 2,0 to 2,4, and 15 to 50 wt.% being part of the copolyetherester, R is a divalent radical remaining after the removal of carboxyl groups from at least one dicarboxylic acid having a molecular weight of less than 300, and D is a divalent radical remaining after the removal of hydroxyl groups from at least one diol having a molecular weight of less than 250, with at least 70 mole% of the dicarboxylic acid employed being either terephthalic acid or 2,6-naphthalene dicarboxylic acid or its ester forming equivalents and at least 70 mole% of the low-molecular weight diol consisting of 1,4-butane diol or its ester forming equivalents, with the sum of the mole percentage of dicarboxylic acid which is neither terephthalic acid nor 2,6-naphthalene dicarboxylic acid or its ester forming equivalents and the mole percentage of low-molecular weight diol which is not 1,4-butane diol or its ester forming equivalents being not more than 30, and the short-chain ester units making up 25-75 wt.% of the copolyetherester,

- b) the hydrophilic polymer which after evaporation of the solvent forms a waterproof, but water vapour permeable coating is made up of a copolyetherester of a similar type and composition as listed under a), with the proviso that preference is given to a polymer of which the melting point is at least 5°C and at most 35°C lower than that of the copolyetherester of which the waterproof film in the laminate is made, and
- c) the organic solvent is selected from the group of halogenated hydrocarbons.

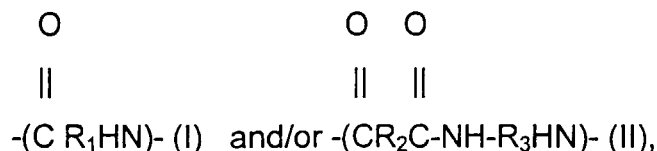
[0011] Copolyetheresters with a reduced melting point can be obtained, int. al., by the incorporation into the short-chain ester units of a dicarboxylic acid other than terephthalic acid or naphthalene dicarboxylic acid having a molecular weight of less than 300 or some other diol having a molecular weight of less than 250. Examples of dicarboxylic acids suitable for use are isophthalic acid and adipic acid. As an example of an alternative low-molecular weight diol to 1,4-butane diol may be mentioned ethylene glycol.

[0012] The halogenated solvents which are preferred according to the present invention can contain fluorine as well as chlorine, bromine or iodine. Since preference is given to solvents with a low boiling point, fluorine- and chlorine-containing solvents are especially eligible for use.

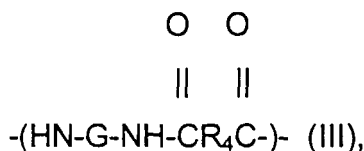
[0013] So far, optimum results have been obtained with the organic solvent used being a chlorinated organic solvent belonging to the group of methylene chloride, chloroform, dichloroethane, trichloroethane, and tetrachloroethane.

[0014] Examples of copolyetheresters suitable for use according to the present invention have been described, int. al., in US-A-4,493,870 and US-A-5,562,977.

[0015] Favourable results can also be obtained when the water vapour permeable, but waterproof film in the laminate is formed by a copolyetheramide composed of polyamide segments A and ethylene oxide groups-containing polyamide segments B, with the polyamide segments A comprising monomer units of the structure:



wherein R₁ stands for an alkylene group having 3 to 11 carbon atoms which may be substituted or not and R₂ and R₃ may be the same or different and stand for a (cyclo)alkylene group having 4 to 11 carbon atoms which may be substituted or not or a difunctional aromatic group, and the polyamide segments B comprising monomer units of the structure:



wherein G stands for a divalent group remaining after the removal of the amino terminated groups of a polyoxyalkylene diamine which is connected or not via one or more lactam units included among the polyamide segments A according to the former formula with a dicarboxylic acid unit wherein R₄ has the meaning of a (cyclo)alkylene group which may be substituted or not, a polyoxyalkylene group or a difunctional aromatic group, with

- α) at least 10 and at most 30 wt.% of the copolyetheramide being made up of ethylene oxide groups,
 β) 30 to 60 wt.% of the copolyetheramide being made up of polyamide segments A and 70 to 40 wt.% being made up of polyamide segments B containing the monomer units according to formula (III), wherein G stands for a polyoxyalkylene group having a molecular weight of 600 to 6000 and an atomic ratio of carbon to oxygen of 2,0 to 4,3, or when the group R₄ stands for a divalent group obtained after removal of the carboxyl groups, for a dimeric fatty acid or for a polyoxyalkylene group having a molecular weight of 600 to 6000 and an atomic ratio of carbon to oxygen of 2,0 to 4,3, as well as for a (cyclo)alkylene group having 2 to 12 carbon atoms which may be substituted or not or for a difunctional aromatic group, and
 γ) the copolyetheramide having a melting point in the range of 180 to 260°C.

[0016] Examples of copolyetheramides suitable for use according to the present invention have been described, int. al, in US-A-5,744,570.

[0017] When a copolyetheramide film is used for the water vapour permeable, but waterproof film in the laminate, favourable results can also be obtained when the selected hydrophilic polymer which after evaporation of the solvent forms a waterproof, but water vapour permeable coating is a copolyetherester of a similar type and composition as indicated above for use as a coating for a hydrophilic copolyetherester film. Also in order to achieve enhanced solubility, preference is again given to a copolyetherester in which the short-chain ester units incorporate a comonomer of low molecular weight. Examples of such comonomers are isophthalic acid, adipic acid, and ethylene glycol. The amount to be incorporated generally corresponds to 5 to 30 mole% of the overall amount of diacid or diol present.

[0018] The invention will be further elucidated with reference to the following examples. Needless to say, the scope of the invention is not restricted to the specific details of the examples.

Example I

[0019] Into a 200 l autoclave were charged 25,95 kg of dimethyl terephthalate, 21,6 kg of 1,4-butane diol, and 12,5 kg of polyethylene oxide glycol having an average molecular weight of 4000. The reaction mixture was heated, with stirring, to 110°C, after which 500 ppm of tetrabutyl titanate (calculated on dimethyl terephthalate) were added. Upon a further increase in temperature to 160°C methanol distilled off, whereupon the pressure was slowly reduced to 100 Pa and the temperature increased to 245°C. In the course of this 3- to 4-hour long polycondensation reaction a product was obtained which had a relative viscosity of 2,76 (determined at a concentration of 1,0 g in 100 g m-cresol at 25°C). The copolyetherester was subjected to a post-condensation in the solid phase until a relative viscosity in the range of 3,5 to 4 was achieved and blow-moulded into a film having a thickness of about 15 µm, followed by lamination with a woven fabric of polyamide 6. Out of the resulting laminate the front and back of a glove were cut. The two parts were sewn together along the edges with the textile sides facing each other to form a three-dimensional lining.

Example II

[0020] In a manner analogous to that indicated in Example I a copolyetherester was prepared starting from 24,1 kg of the dimethylester of 2,6-naphthalene dicarboxylic acid (DM-2,6-NDC), 13,3 kg of 1,4-butane diol, 12,0 kg of polyethylene oxide glycol having an average molecular weight of 2000, and 12,0 kg of polytetramethylene oxide glycol (pTHF) having an average molecular weight of 1000. The reaction was carried out in the presence of 24,1 g of tetrabutyl titanate and 0,25 kg of 1,3,5-trimethyl-2,4,6-tris[3,5-di-tert.butyl-4-hydroxybenzyl] as anti-oxidant and 250 g of SiO₂ (as suspension in 1,4-butane diol). The polymerisation temperature was 246°C. The product had a relative dissolving viscosity of 2,50 (determined at a concentration of 1,0 g in 100 g m-cresol at 25°C). Post-condensation in the solid phase yielded a product having an $\eta_{rel} = 4,32$.

The percentage by weight of short-chain ester units was 43,2, which corresponds to a percentage by weight of long-chain ester units of 56,8. This copolyetherester was cast to form a foil having a thickness of 13,5 µm, which was then laminated with a woven fabric of polyamide-6.

Example III

[0021] In a manner analogous to that indicated in Example I, making use of 465 kg of dimethyl terephthalate, 82 kg of dimethyl isophthalate, 490 kg of polytetrahydrofuran having a molecular weight of 1000, and 350 kg of polyethylene oxide glycol having a molecular weight of 2000, a copolyetherester was prepared which contained 33,8 wt.% of short-chain ester units.

The thus prepared copolyetherester was processed into an 8 wt.% solution in methylene chloride.

Example IV

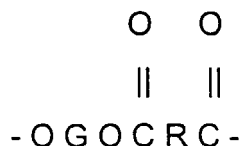
[0022] With the fingers pointing down, the lining made in Example I, with the copolyetherester film turned outward, was dipped three times for 15 seconds each in the methylene chloride solution of Example III. In the intermediate periods of 45 seconds each evaporation of the solvent took place. During this evaporation process proceeding at room temperature the lining was turned 180°, such that on conclusion of the evaporation process the fingers were pointing upwards. Afterwards, the lining was filled completely with water to check its impermeability to water. If there was no leakage after 10 minutes, the lining was characterised as waterproof.

The waterproofness of the lining was amply sufficient.

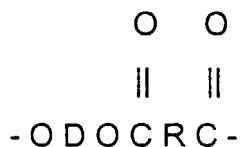
Claims

1. A process for sealing the seams of a waterproof, water vapour permeable article comprising a waterproof, water vapour permeable film and having seams, characterised in that a surface of the article is contacted at least at the seams of the film with a coating solution of a hydrophilic polymer in an organic solvent which acts as a swelling agent for the waterproof, water vapour permeable film, after which the solvent is evaporated.
2. A process according to claim 1, characterised in that the contacting comprises dipping the film into the coating solution.
3. A process according to claim 1, characterised in that the article is a lining comprising a laminate of the waterproof, water vapour permeable film and a textile material.
4. A process according to claim 3, characterised in that the method further comprises, prior to the contacting step, joining together along contours of a material to be lined one or more sections of the lining in which textile sides of the lining are facing one another.
5. A process according to claim 3, characterised in that the seams of the lining are formed towards an inside portion of the lining, and the contacting comprises turning the lining inside out to expose the portion of the lining where the seams are, and dipping this portion into the coating solution.
6. A process according to claim 1, characterised in that

a) the waterproof, but water vapour permeable film takes the form of a copolyetherester consisting of a plurality of recurrent intralinear long-chain ester units and short-chain ester units randomly joined head to tail through ester bonds, the long-chain ester units corresponding to the formula:



and the short-chain ester units corresponding to the formula:



wherein G is a divalent radical remaining after the removal of terminal hydroxyl groups from at least one long-chain glycol having an average molecular weight in the range of 600 to 4000 and an atomic ratio of carbon to oxygen in the range of 2,0 to 4,3, at least 20 wt.% of the long-chain glycol having a carbon to oxygen ratio in the range of 2,0 to 2,4, and 15 to 50 wt.% being part of the copolyetherester, R is a divalent radical remaining after the removal of carboxyl groups from at least one dicarboxylic acid having a molecular weight of less than

300, and D is a divalent radical remaining after the removal of hydroxyl groups from at least one diol having a molecular weight of less than 250, with at least 70 mole% of the dicarboxylic acid employed being either terephthalic acid or 2,6-naphthalene dicarboxylic acid or its ester forming equivalents and at least 70 mole% of the low-molecular weight diol consisting of 1,4-butane diol or its ester forming equivalents, with the sum of the mole percentage of dicarboxylic acid which is neither terephthalic acid nor 2,6-naphthalene dicarboxylic acid or its ester forming equivalents and the mole percentage of low-molecular weight diol which is not 1,4-butane diol or its ester forming equivalents being not more than 30, and the short-chain ester units making up 25-75 wt.% of the copolyetherester,

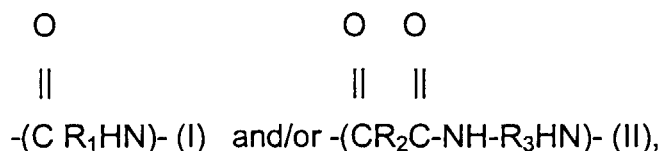
b) the hydrophilic polymer which after evaporation of the solvent forms a waterproof, but water vapour permeable coating, is made up of a copolyetherester of a similar type and composition as listed under a), and

c) the organic solvent comprises one or more halogenated hydrocarbons.

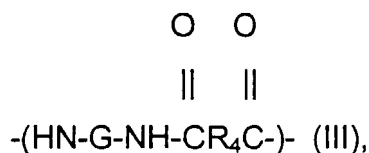
7. A process according to claim 6, characterised in that the melting point of the copolyetherester of the waterproof, water vapour permeable coating is at least 5°C and at most 35°C lower than that of the copolyetherester of which the waterproof film is made.

8. A process according to claim 1, characterised in that the organic solvent used is a chlorinated organic solvent selected from the group of methylene chloride, chloroform, dichloroethane, trichloroethane, and tetrachloroethane.

9. A process according to claim 1, characterised in that the waterproof, water vapour permeable film comprises a copolyetheramide composed of polyamide segments A and ethylene oxide groups-containing polyamide segments B, with the polyamide segments A comprising monomer units of the structure:



wherein R₁ stands for an alkylene group having 3 to 11 carbon atoms which may be substituted or not and R₂ and R₃ may be the same or different and stand for a (cyclo)alkylene group having 4 to 11 carbon atoms which may be substituted or not or a difunctional aromatic group, and the polyamide segments B comprising monomer units of the structure:



wherein G stands for a divalent group remaining after the removal of the amino terminated groups of a polyoxyalkylene diamine which is connected or not via one or more lactam units included among the polyamide segments A according to the former formula with a dicarboxylic acid unit wherein R₄ has the meaning of a (cyclo)alkylene group which may be substituted or not, a polyoxyalkylene group or a difunctional aromatic group, with

α) at least 10 and at most 30 wt.% of the copolyetheramide being made up of ethylene oxide groups,

β) 30 to 60 wt.% of the copolyetheramide being made up of polyamide segments A and 70 to 40 wt.% being made up of polyamide segments B containing the monomer units according to formula (III), wherein G stands for a polyoxyalkylene group having a molecular weight of 600 to 6000 and an atomic ratio of carbon to oxygen of 2,0 to 4,3, or when the group R₄ stands for a divalent group obtained after the removal of the carboxyl groups, for a dimeric fatty acid or for a polyoxyalkylene group having a molecular weight of 600 to 6000 and an atomic ratio of carbon to oxygen of 2,0 to 4,3, as well as for a (cyclo)alkylene group having 2 to 12 carbon atoms which may be substituted or not or for a difunctional aromatic group, and

γ) the copolyetheramide having a melting point in the range of 180 to 260°C.

10. A waterproof, water vapour permeable article comprising a waterproof, water vapour permeable film having seams

and comprised of at least a waterproof, water vapour permeable film and a waterproof, water vapour permeable hydrophilic polymer coating upon the waterproof, water vapour permeable film over at least the seams of the film, the article being produced by a method comprising:

5 contacting a surface of the article at least at the seams of the film with a coating solution containing a hydrophilic polymer in an organic solvent which acts as a swelling agent for the waterproof, water vapour permeable film, and
evaporating the organic solvent to form the waterproof, water vapour permeable hydrophilic polymer coating.

10 **11.** A waterproof, water vapour permeable article comprising a waterproof, water vapour permeable film having seams and comprised of at least a waterproof, water vapour permeable film and a waterproof, water vapour permeable hydrophilic polymer coating upon the waterproof, water vapour permeable film over at least the seams of the film.

12. A waterproof, water vapour permeable article according to claim 11, wherein

15 a) the waterproof, but water vapour permeable film takes the form of a copolyetherester consisting of a plurality of recurrent intralinear long-chain ester units and short-chain ester units randomly joined head to tail through ester bonds, the long-chain ester units corresponding to the formula:



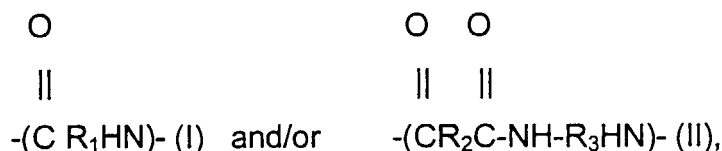
and the short-chain ester units corresponding to the formula:



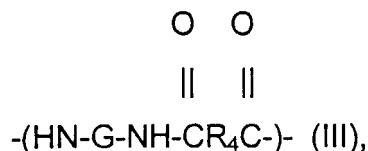
wherein G is a divalent radical remaining after the removal of terminal hydroxyl groups from at least one long-chain glycol having an average molecular weight in the range of 600 to 4000 and an atomic ratio of carbon to oxygen in the range of 2,0 to 4,3, at least 20 wt.% of the long-chain glycol having a carbon to oxygen ratio in the range of 2,0 to 2,4, and 15 to 50 wt.% being part of the copolyetherester, R is a divalent radical remaining after the removal of carboxyl groups from at least one dicarboxylic acid having a molecular weight of less than 300, and D is a divalent radical remaining after the removal of hydroxyl groups from at least one diol having a molecular weight of less than 250, with at least 70 mole% of the dicarboxylic acid employed being either terephthalic acid or 2,6-naphthalene dicarboxylic acid or its ester forming equivalents and at least 70 mole% of the low-molecular weight diol consisting of 1,4-butane diol or its ester forming equivalents, with the sum of the mole percentage of dicarboxylic acid which is neither terephthalic acid nor 2,6-naphthalene dicarboxylic acid or its ester forming equivalents and the mole percentage of low-molecular weight diol which is not 1,4-butane diol or its ester forming equivalents being not more than 30, and the short-chain ester units making up 25-75 wt.% of the copolyetherester, and

50 b) the hydrophilic polymer which after evaporation of the solvent forms a waterproof, but water vapour permeable coating, is made up of a copolyetherester of a similar type and composition as listed under a).

13. A waterproof, water vapour permeable article according to claim 11, wherein the waterproof, water vapour permeable film comprises a copolyetheramide composed of polyamide segments A and ethylene oxide groups-containing polyamide segments B, with the polyamide segments A comprising mono-
55 mer units of the structure:



wherein R_1 stands for an alkylene group having 3 to 11 carbon atoms which may be substituted or not and R_2 and R_3 may be the same or different and stand for a (cyclo)alkylene group having 4 to 11 carbon atoms which may be substituted or not or a difunctional aromatic group, and the polyamide segments B comprising monomer units of the structure:



wherein G stands for a divalent group remaining after the removal of the amino terminated groups of a polyoxyalkylene diamine which is connected or not via one or more lactam units included among the polyamide segments A according to the former formula with a dicarboxylic acid unit wherein R_4 has the meaning of a (cyclo)alkylene group which may be substituted or not, a polyoxyalkylene group or a difunctional aromatic group, with

- α) at least 10 and at most 30 wt.% of the copolyetheramide being made up of ethylene oxide groups,
- β) 30 to 60 wt.% of the copolyetheramide being made up of polyamide segments A and 70 to 40 wt.% being made up of polyamide segments B containing the monomer units according to formula (III), wherein G stands for a polyoxyalkylene group having a molecular weight of 600 to 6000 and an atomic ratio of carbon to oxygen of 2,0 to 4,3, or when the group R_4 stands for a divalent group obtained after the removal of the carboxyl groups, for a dimeric fatty acid or for a polyoxyalkylene group having a molecular weight of 600 to 6000 and an atomic ratio of carbon to oxygen of 2,0 to 4,3, as well as for a (cyclo)alkylene group having 2 to 12 carbon atoms which may be substituted or not or for a difunctional aromatic group, and
- γ) the copolyetheramide having a melting point in the range of 180 to 260°C.

14. A waterproof, water vapour permeable article according to claim 11, wherein the waterproof, water vapour permeable article is shaped as a glove, garment or shoe.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 2401

DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	CH 677 584 A (BULLSON) 14 June 1991 (1991-06-14) * claims *	1
A	EP 0 410 291 A (GORE, W.L.) 30 January 1991 (1991-01-30) * claims; example 1 *	1
A	WO 92 05308 A (LANTOR) 2 April 1992 (1992-04-02) * page 3, line 10 - line 14; claims *	1
The present search report has been drawn up for all claims		
Place of search		Date of completion of the search
THE HAGUE		4 November 1999
		Examiner
		Hellemans, W
<p>CLASSIFICATION OF THE APPLICATION (Int.Cl.7)</p> <p>D06M23/18</p> <hr/> <p>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</p> <p>D06M A41D</p>		
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>		

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 20 2401

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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04-11-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CH 677584	A	14-06-1991	NONE	
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